Q7.6

For rotation in three dimensions, the angular momentum vector has three components whose corresponding operators do not commute. This indicates that all three components of the angular momentum can't be known simultaneously. Therefore, the angular momentum vector can't lie on the z axis, because this requires that the x and y components are known to be zero.

Q7.12

There is nothing special about the z direction. The coordinate system could be rotated to align any direction along the z direction. At any time, only one component of angular momentum and its magnitude can be known and the z direction is chosen because the angular momentum operator for this component has a simple form.

P7.2

a)

$$\mathbf{l} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \boldsymbol{i}\begin{vmatrix} y & z \\ p_y & p_z \end{vmatrix} - \boldsymbol{j}\begin{vmatrix} x & z \\ p_x & p_z \end{vmatrix} + \boldsymbol{k}\begin{vmatrix} x & y \\ p_x & p_z \end{vmatrix}$$

$$= \boldsymbol{i}(yp_z - zp_y) - \boldsymbol{j}(xp_z - zp_x) + \boldsymbol{k}(xp_y - yp_x)$$

b)

$$l_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$l_y = +i\hbar\left(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right)$$

$$l_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

c)

$$\begin{aligned}
[l_x, l_y] &= (l_x l_y - l_y l_x) f \\
&= \left(-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right)\left(i\hbar\left(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right)f\right) \\
&\quad - \left(i\hbar\left(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right)\right)\left(-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)f\right) \\
&= \hbar^2\left(\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(x\frac{\partial f}{\partial z} - z\frac{\partial f}{\partial x}\right)\right) - \hbar^2\left(\left(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right)\left(y\frac{\partial f}{\partial z} - z\frac{\partial f}{\partial y}\right)\right) \\
&= \hbar^2\left(\left(y\frac{\partial}{\partial z}x\frac{\partial f}{\partial z} - y\frac{\partial}{\partial z}z\frac{\partial f}{\partial x} - z\frac{\partial}{\partial y}x\frac{\partial f}{\partial z} + z\frac{\partial}{\partial y}z\frac{\partial f}{\partial x}\right)\right. \\
&\quad \left. - \left(x\frac{\partial}{\partial z}y\frac{\partial f}{\partial z} - x\frac{\partial}{\partial z}z\frac{\partial f}{\partial y} - z\frac{\partial}{\partial x}y\frac{\partial f}{\partial z} + z\frac{\partial}{\partial x}z\frac{\partial f}{\partial y}\right)\right)
\end{aligned}$$

$$\begin{aligned}
= \hbar^2&\left(\left(yx\frac{\partial^2 f}{\partial z^2} - y\frac{\partial f}{\partial x} - yz\frac{\partial^2 f}{\partial z\partial x} - zx\frac{\partial^2 f}{\partial y\partial z} + z^2\frac{\partial^2 f}{\partial y\partial x}\right)\right. \\
&\quad \left. - \left(yx\frac{\partial^2 f}{\partial z^2} - x\frac{\partial f}{\partial y} - xz\frac{\partial^2 f}{\partial z\partial y} - zy\frac{\partial^2 f}{\partial x\partial z} + z^2\frac{\partial^2 f}{\partial x\partial y}\right)\right)
\end{aligned}$$

$$= \hbar^2\left(-y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}\right) = i\hbar l_z$$

P7.11

$$\langle p_x^2\rangle = \int_{-\infty}^{\infty} \psi_x^*\left(-\hbar^2\frac{d^2}{dx^2}\right)\psi_x dx$$

n=0

$$\psi = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\alpha x^2} \Rightarrow \langle p_x^2\rangle = -\hbar^2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\int_{-\infty}^{\infty} e^{-\frac{1}{2}\alpha x^2}\frac{d^2}{dx^2}e^{-\frac{1}{2}\alpha x^2}dx =$$

$$\begin{aligned}
&= -\hbar^2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\int_{-\infty}^{\infty} e^{-\frac{1}{2}\alpha x^2}(\alpha^2x^2 - \alpha)e^{-\frac{1}{2}\alpha x^2}dx = -\hbar^2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\int_{-\infty}^{\infty} e^{-\alpha x^2}(\alpha^2x^2 - \alpha)dx \\
&= -\hbar^2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\int_{-\infty}^{\infty}(\alpha^2x^2 - \alpha)e^{-\alpha x^2}dx = -\hbar^2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\left(2\alpha^2\frac{1}{4\alpha}\sqrt{\frac{\pi}{a}} - 2\,\alpha\frac{1}{2}\sqrt{\frac{\pi}{a}}\right) \\
&= -\hbar^2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\left(\alpha\frac{1}{2}\sqrt{\frac{\pi}{a}} - \alpha\sqrt{\frac{\pi}{a}}\right) = \hbar^2\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\left(\frac{\alpha}{2}\sqrt{\frac{\pi}{a}}\right) = \frac{1}{2}\hbar^2\alpha
\end{aligned}$$

n=1

$$\psi = \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{4}} x e^{-\frac{1}{2}\alpha x^2} \Rightarrow \langle p_x^2 \rangle = -\hbar^2 \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} x e^{-\frac{1}{2}\alpha x^2} \frac{d^2}{dx^2} x e^{-\frac{1}{2}\alpha x^2} dx$$

$$= -\hbar^2 \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} (\alpha^2 x^4 - 3\alpha x^2) e^{-\alpha x^2} dx = -\hbar^2 \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{2}} \left(\frac{3}{4}\sqrt{\frac{\pi}{a}} - \frac{6}{4}\sqrt{\frac{\pi}{a}}\right)$$

$$= -\hbar^2 \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{2}} \left(-\frac{3}{4}\right)\left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}} = \frac{3}{2}\hbar^2 \alpha$$

n=2

$$\psi = \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{4}} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} \Rightarrow \langle p_x^2 \rangle = -\hbar^2 \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} \frac{d^2}{dx^2} (2\alpha x^2 - 1) e^{-\frac{1}{2}\alpha x^2} dx$$

$$= -\hbar^2 \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} (2\alpha x^2 - 1)(2a^3 x^4 - 11a^2 x^2 + 5a) e^{-\alpha x^2} dx$$

$$= -\hbar^2 \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} (4a^4 x^6 - 24a^3 x^4 + 21a^2 x^2 - 5a) e^{-\alpha x^2} dx$$

$$= -\hbar^2 \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{2}} \left(\frac{15}{2}a - 18a + \frac{21}{2}a - 5a\right)\left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}} = -\hbar^2 \frac{1}{2}(-5a) = \frac{5}{2}\hbar^2 \alpha$$

Note that we used the following standard integrals:

$$\int_0^{\infty} x^{2k} e^{-ax^2} dx = \frac{(2k-1)!!}{2^{k+1} a^k} \sqrt{\frac{\pi}{a}}$$

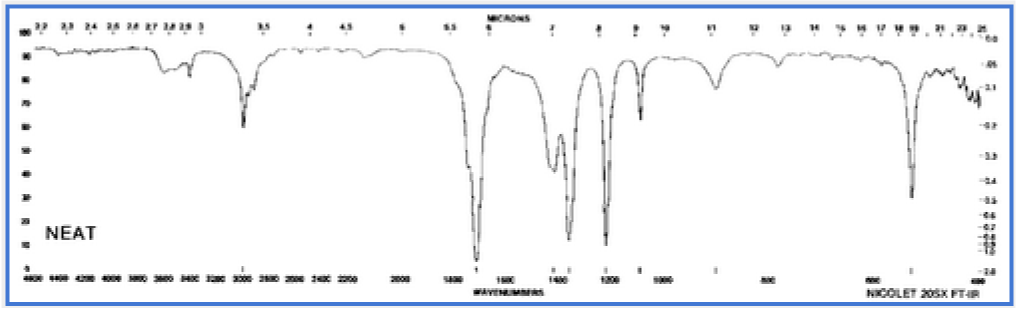
$$\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

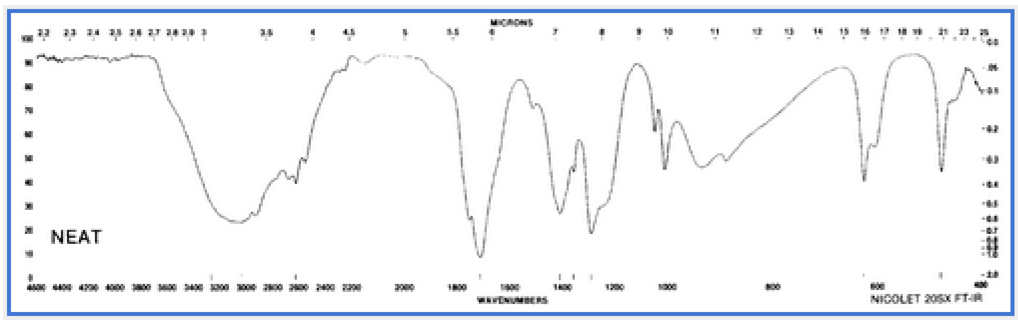
**P8.4**

No peak around 600-800 (C-Cl), 3300-3500 (N-H), 3450-3650 (O-H).

A strong peak around 1750 (C=O stretch), and other peaks at 1250 (C-C stretch), 1500 (C-H bend) and 3000 (C-H stretch).

Therefore the molecule is most likely $(CH_3)_2CO$. For comparison, the real IR spectrum of acetone and acetic acid are shown below respectively (from http://www.bluffton.edu/~bergerd/classes/cem222/infrared/oxygen.html):




**P8.5**

For triatomic linear rotor (A-B-C):

$$I = m_A r_1^2 + m_C r_2^2 - \frac{(m_A r_1 - m_C r_2)^2}{m_A + m_B + m_C}$$

Where $r_1$ and $r_2$ are distances between A,B and B,C respectively. So for the OCS molecule:

$$r_1 = O - S,\ \ r_2 = C - S$$

(Note that we assume that the C-S distance is the same between the two molecules and the slightly heavier 34S doesn't increase the C-S distance in the second molecule).

$$m_{O_{16}} = A = 15.995\ amu\ ,\ \ m_{C_{12}} = B = 12.000\ amu,$$

$$m_{S_{32}} = C = 31.972\ amu,\ \ m_{S_{34}} = D = 33.968\ amu$$

$$\frac{h}{8\pi^2 \times 6081.490 \times 10^6} = Ar_1^2 + Cr_2^2 - \frac{(Ar_1 - Cr_2)^2}{A + B + C}$$

$$\frac{h}{8\pi^2 \times 5932.816 \times 10^6} = Ar_1^2 + Dr_2^2 - \frac{(Ar_1 - Dr_2)^2}{A + B + D}$$

Now we have two equations and two variables ($r_1$ and $r_2$). After solving these two equations using a software (such as MATLAB or Excel) the two distances are:

$$r_1 = 116.241\ pm$$

$$r_2 = 156.003\ pm$$